Use of Natural Fat Emulsions in Fatliquoring Process and Investigation of Fatty Spue Formation

by

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Abstract

Fatty spew is one of the most frequently defects appearing on finished leathers, especially sheepskins. Origins of this problem include an insufficient degreasing process, presence of excess residual natural fat in leather, quantity and quality of fatliquoring material added during the fatliquoring process and defective fatliquoring techniques. It is usually not easy to identify this problem during the processes. The aim of this study is to find out the limit value of natural fat that cause to fatty spew and its effect on leather quality. In the experiments Irish ovine sheepskins were used, as they are known for their high natural fat content. The experiments were carried out in three groups. The first group was processed without degreasing and fatliquoring. The second group was degreased and processed without fatliquoring and the third group was degreased; and fatliquored with 3, 5 and 7% of their own emulsified fat. The application of 3% fat emulsion is agreeable due to fatty spew formation in 5% and 7% fat emulsion application, as expected from preliminary tests. Some physical and chemical characteristics of natural and emulsified fats were investigated such as density, acid, peroxide and iodine values. Visual images of skin surfaces were obtained by Scanning Electron Microscopy (SEM). Gas Chromatography (GC), Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FT-IR). Analyses were performed for the determination of fatty acids components that cause fatty spew defect. It was determined that double bond between C and C in the structure of the palmitoleic and linoleic acids was saturated, the ratio of palmitic and stearic acids was increased and palmitic and stearic acids were found to be the main reasons for fatty spew formation.

Resumen

Efloraciones grasosas es uno de los más frecuentes defectos que resultan en cueros terminados, especialmente en los producidos con pieles de oveja. Los orígenes de este problema incluirían un insuficiente proceso de desengrase, la presencia excesiva de grasa residual natural, la cantidad y calidad del material utilizado en el proceso del engrase mismo, y por técnicas defectuosas de engrase. A menudo no es fácil la detección del problema durante el proceso mismo. El objeto del estudio fue determinar el valor límite de grasa natural que resulta en efloraciones de grasa y sus efectos sobre la calidad del cuero. En los experimentos se utilizaron pieles ovinas irlandesas, siendo estas reconocidas por su alto contenido de grasa natural. Se efectuaron los experimentos en tres grupos. El primero se proceso sin desengrase así como también sin engrasar adicionalmente. El segundo grupo se procesó desengrasando pero sin ningún reengrase. Las del tercer grupo se procesaron desengrasando; y se engrasaron con 3, 5 y 7% de su mismo tipo grasa, pero emulsionada. El ofrecimiento de 3% fue favorable debido que preliminarmente ya se había determinado que el ofrecer 5% o 7% de la grasa emulsionada resultaría en efloraciones. Varias características de grasa natural como también la emulsionada se investigaron, tales como la densidad, los valores de los índices numéricos de ácido, de yodo y de peróxido. Imágenes de las superficies fueron obtenidas por medio de Microscopía por Barrido Electrónico (SEM). [Adicionalmente] Cromatografía Gaseosa (GC), Resonancia Magnética Nuclear (NMR) y Espectroscopía Infrarroja por Transformaciones de Fourier (FT-IR) [se efectuaron]. Análisis fueron efectuados para determinar los componentes de ácidos grasos que causan el defecto de efloraciones grasosas. Se ha establecido que los enlaces dobles entre carbonos en las estructuras de ácidos palmitoleico y linoleico fueron saturados, incrementando la proporción de los ácidos palmítico y esteárico y que estos son la causa principal de la formación de efloraciones grasosas.

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Manuscript received April 18, 2010, accepted for publication September 28, 2010

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INTRODUCTION

The term lipid has traditionally been used to describe a wide variety of natural products including fatty acids and their derivatives, steroids terpens, carotenoids and bile acids.[1] Natural oils and fats are the main sources of fatliquors in the leather industry. The skins obtained from sheeps, goats and pigs can contain considerable amount of natural fat, in some skin areas increase up to 30% based on dry matter.[2] It is well known that unevenly distributed high amount of fat has to be removed during the early tanning stages.[3] During the preliminary process of unhairing and bating, the natural fat starts to be removed from the skin; this process continues with degreasing.[4,5] For an effective degreasing, fats have to be removed from fiber structure and the rest well distributed in cross-section. This depends on convenient surface active agents, temperature, washing out and also enzyme application.[6,7]

The natural fats of skins/hides or used fatliquoring substance can cause many problems on finished leathers such as grease stains, uneven tanning,[8] uneven coloring, soaps[9] and fat spew.[10] Considering the fatty spew defect, high content of natural fat in the leather due to inadequate degreasing, introduction of fatty substances having large amounts of free saturated and unsaturated fatty acids are the main reasons.[11] Fatty spew is promoted by storage under alternating temperature conditions, high humidity, inadequate neutralization and by microbial action on grain and flesh side of the leather, on shoes or other leather articles.[11,12] In addition to this reasons, certain types of dyes and mordants for dyes have an influence on fatty spew formation.[13] Mostly the fatty spew distributed over the entire leather surface but sometimes also it could be occurred only in parts.[11,12] When spew is caused by natural fat, the spew is not uniform in distribution but when a fatliquor component spews, the spew is generally uniformly present over the whole surface of the leather. White, crystalline coating or light film occurs on dried and finished leather, mainly on mineral tanned leathers for this defective area; contact with an open flame will melt this coating in contrast to the defect caused by salt. Lastly, the type of tanning also affects the spew formation; for example vegetable-tanned leathers were less prone to spew formation than chromium tanned leathers.[14]

The main purpose of fatliquoring is to prevent the final product from having a thin and dry handle and to minimize fibril adhesion during drying. Usually care is taken not to introduce too much because under the action of any acids which might be present in the leather, fatty spew may deposit on the surface. Thus fatty spew is also derived from fatty materials used to lubricate the leather[11,12] and it is well known that sulphated, sulphonated, sulphited and phosphated fat as well as mixtures of neutral fat with different emulsifiers are used to obtain fatliquoring emulsions to lubricate leather.[15-17] Triglycerides which form free fatty acids are frequently the cause of the trouble also indicate that spews are solid fatty acids or tri-glycerides, but more viscous and resinous forms occasionally arise from the oxidative polymerization of unsaturated components. In addition to this, microcrystalline wax, polyethylene glycol esters, and amides, the latter substance being prepared from stearic and palmitic acids and being used in cationic topping oils, may cause fatty spew defect. Less viscous oils that are incorporated into lubricating products for leather have the ability of carrying waxes, esters, and amides to the surface of the leather.[13] This paper reports the effect of emulsified natural fat on fatty spew formation by finding out the limit value of emulsified natural fat that cause fatty spew and investigation of its characteristic the same properties as far as origin.

EXPERIMENTAL

Material

Twenty five Irish type sheepskins having a high fat content were used in the research. Skin samples were chosen randomly, but paying attention that they have the same properties like origin, sex, age and weight. As a fatliquoring material, natural fat was extracted from sheepskins and converted into emulsified material using additives shown at Table I. For preparation of emulsified fat, first skins were treated in accordance with ISO 2419[18] and the fat in skin samples was extracted according to ISO 4048.[19] Conventional chemicals were used in garment leather manufacturing.

Method

After the sheepshin degreasing process, further processing usual processing steps were applied until fatliquoring. At fatliquoring step of the process, the emulsified natural fat was applied in different ratios of 3, 5 and 7%. All skin samples were dyed with black dyestuff to observe the fat spew better and after drying and the leather samples were kept in the refrigerator at 0°C. As a control group, skins were processed

TABLE I
Emulsification recipe for natural fat[18]

Substance	Proportion (%)
Natural fat	60
Neutralization substance	1
Surface active substance	4
Stabilization substance	0,5
Bactericide	0,05
Completed with water to 100	

TABLE II

Conventional recipe used fat emulsion in fatliquoring process

Process	Ratio (%)	Substance			Time (min.)
Degreasing	4	Non-ionic surfactant			60
Washing	100	Water	30°C		
	3°Be	Salt			15
		Washing less four times			
Pickle	100	Water	28°C		
	6°Be	Salt			5
	+1,2	Formic Acid			20
	+0,8	Sulphuric Acid			75
				pH 2,9	
Tanning	+3	Chromium Tanning Agent			45
	+3	Chromium Tanning Agent			30
	+1	Basification Agent			10
	+2	Chromium Tanning Agent			360
				pH 4,0	
		Horsing up and waiting for two days and shaving			
Neutralization	100	Water	30°C		
	0,2	Formic Acid			15
	+3	Chromium Syntan			60
	+3	Mimosa			60
	+1	Black Dyestuff	45°C		30
	+1	Black Dyestuff			30
	+x	Fat Emulsion	50°C		
	+0,8	Formic Acid			30
		Washing with water		pH 4,2	

without degreasing and fatliquoring until wet end process in order to observe the formation of fatty spew. The applied conventional garment leather manufacturing process is can be seen at Table II.

Determination of Fat Content

Solvent Extraction System (SES) was used which can reduce extraction time and solvent consumption and yields equivalent results. Prior to analysis, leather samples were prepared in accordance with TS EN ISO 4044.[21] Subsequently, samples were loaded into the SES system and dichloromethane (Merck) was pumped into an extraction cell which is then pressurized and heated for several minutes. Test materials were dipped into solvent and left for 100 minutes at 80°C and solvent was circulated after placing them in the cartridge. They were then taken out and the solvent phase was separated from the fatty material using a vacuum system.

Acid, Iodine and Peroxide Values

Determination of iodine, peroxide and acid values of fats were performed following the standards TS 4961 EN ISO 3961[22] and TS 4964 ISO 3960.[23]

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) produce images of surface by interaction of an electron beam with the sample. The morphology of the leather samples were observed by SEM techniques, which allowed the comparison of different physical properties such as the images of fatty spew and pore. Samples were cut along the cross section for viewing running parallel to the direction of hair follicles.[24,25] Chromium tanned samples were not fixed with aldehydes owing to the fixing effect. Osmium tetroxide was used for fixing fat or fatliquoring substances due to its protection of tissue and fixation of fatty substance.[26,27] Samples were washed with phosphate buffer solution to remove primer fixative substance. After this step water was removed with ethyl alcohols with different concentrations from 70% to absolute. Finally, hexamethylenedisilazan was used in order to dry the samples and constitute silyl esters which have more hydrogen atoms like glucose, amino acid and alcohol.

Gas Chromatography (GC) Analysis

The natural fats of sheep skins have some common characteristics and gas chromatography (GC) is probably the most popular and effective technique to analyze fats and fatty spew. Amounts of volatile organics such as fatty acids and their methyl esters can easily be analyzed qualitatively and quantitatively with this technique.[28,29] GC analysis was carried out on an Agilent 6890 gas chromatography operated with an injector and data were acquired by solution software. The GC experimental conditions were given at Table IV. Hydrolysis or saponification of lipid is required, therefore the sheepskin natural fat is transesterified to produce esters prior to analysis, according to TS 4504 EN ISO 5509[30] and analyzed with TS 4664 EN ISO 5508.[31] Fatty spew that entirely constituted of saturated fatty acids are characterized; probably the hydrolysis of the triglycerides in leather causes fatty spew.[32]

C Nuclear Magnetic Resonance (NMR)

Magnetic resonance spectroscopy deals with transitions between the levels which a magnetic dipole can occupy in a magnetic field and this technique can safely be used to find out the quantities of fatty acid contents, providing data as reliable as those obtained by other techniques such as GC.[33] All functional groups give absorption lines. Positional distribution of fatty acids esterified to the glycerol molecule in triacylglycerols may be detected directly.[34] The C NMR spectra of the most important saturated and mono- and polyunsaturated fatty acids found in lipids have been interpreted.[35] Whereas NMR spectroscopy gives information about arrangement of hydrogenes in a molecule, C NMR gives information about the carbon skeleton. NMR analyses were performed on samples taken from fatty spew observed leathers. In the present study, solution C NMR spectrum was recorded for 300 scans at 30°C for 0.08 g of sample that dissolved in 1.0 mL $CDCl_3$ in 5 mm NMR tube. A 70° pulse flipping angle, a 10 µs pulse width, and a 15 second delay time between scans were used. C spectra were recorded at 75 MHz. Resonances were assigned by adding pure tri acyl glyceride standards palmitic acid and stearic acid obtained from Sigma Chemical Co. The NMR method was also calibrated by measuring a series of two standard fatty acids palmitic and stearic acid samples. As a reference material for analysis, palmitic acid and stearic acid were purchased from Fluka.

TABLE IV

GC experimental conditions

Column	SUPELCO SP-2380
Type of Column	Silica Capillary Column
Length of Column	60 m
Diameter and Thickness of Column	0,25 mm-0,2 µm
Injection	Split/splitless
Type of Detector	FID
Temperature of Detector	300°C
Inlet Temperature and Pressure	250°C, 100 kPa
Oven temperature program	50°C-280°C at 3°C/min.
Flow	0,5 ml/min.
Carrier Gas	Helium
Split Ratio	1:100
Injection Volume	1,0 µl
Column Flow	0,5 µl
Hydrogen Flow	50 ml/min.
Air Flow	400 ml/min
Time of Analysis	45 min.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

ATR crystals are generally transparent above 600 cm^{-1} and have high refractive index of the sample medium [36]. In the study, Perkin Elmer Spectrum 100 with ATR device was used for FTIR analysis and extracted natural fat from skin samples and fat which was removed from the fatty spew area were dissolved in a volatile solvent which was evaporated from drops placed on salt plates. Besides this, the areas with and without fatty spew formation were also tested by transmitted light IR spectra using the spectrum library. Pressure was not used on the sample to contact the crystal because of its liquid characteristic. The ATR crystal was carefully cleaned with pure methanol to eliminate the presence of oil/fat residues for each sample. FTIR data of the samples were collected by co-adding 4 scans at a resolution of 4 cm^{-1} over the region 4000–700 cm^{-1}. All spectra were rationed against a background air spectrum and stored as absorbance values at each data point.

RESULTS AND DISCUSSION

Fat Content of Skin and Formation of Fat Spew

The matters soluble in dichloromethane of skins before and after degreasing process were determined as 17.45% and 1.98% respectively. When emulsified natural fat was used as fatliquoring agent, the limit value of natural fat caused fatty spew was found as 3%, which means that natural fat emulsion can be used safely up to 3%. Fatty spew formation was also observed for the leathers which used 5 and 7% of emulsified natural fat.

Acid, Iodine and Peroxide Values

Acid, iodine and peroxide value for natural fat and fat emulsion can be seen at Table III. When temperature was cooled down the viscosity of oxidized oil increased and this indicates the possibility of polymerization caused by free radicals and conjugated double bonds in the oxidation process.[37] It was found that the peroxide values of the natural fat and fat emulsion were close, but the peroxide value of fat emulsion was less than natural fat. Iodine values are used to indicate the degree of unsaturation and for animal fats this value is usually within the range 35-70.[12] The iodine degree of natural fat obtained from sheep skins and its emulsified fat were found in this range. Acid value of the fat emulsion was less than natural fat because of the added neutralization substance during emulsification process. Iodine index of the fat emulsion was expected to be lower than natural one but it was found a little bit higher than the reference data.[38]

Scanning Electron Microscopy (SEM)

Figures 1, 2 and 3 were taken from the leather surface areas where fatty spew formation was observed and their magnification were 2000X for figure 2 and 4 while figure 3's magnification was 750X. Natural fat particles can be clearly seen from the micrograph shown in Figure 2. Also it was seen from Figure 3 that the fatty spew covered the leather surface like a layer and the color of these areas shown in figure 2 and 3 were whiter than the areas which fatty spew formation was not seen. The emulsified sulphated oil is deposited as globules of oil which is largely immobile when the leather is wet, because the carrier, the sulphated fraction, is no longer available to transport the neutral oil like a natural fat emulsion which was used in this study.[39]

TABLE III

Acid, Iodine index and peroxide value for natural fat and fat emulsion.

	Acid Value	Iodine Value	Peroxide Value
Natural Fat	10.55	47	8.77
Fat Emulsion	10.00	54	7.70

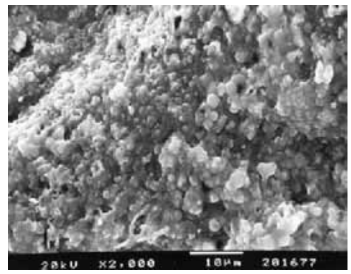

Figure 1: SEM micrograph of fatty spue on leather surface (*2000)

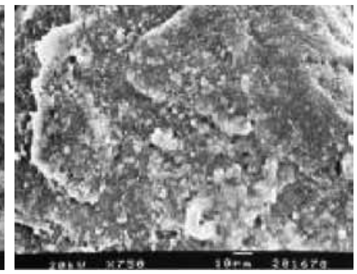

Figure 2: SEM micrograph of fatty spue on leather surface (*750)

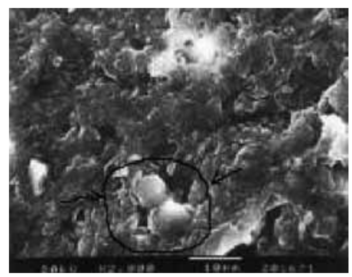

Figure 3: Displays of fatty spue micrograph on leather surface (*2000)

Gas Chromatography (GC) Analysis

GC chromatograms of natural fat and fatty spews are presented in Figure 4.

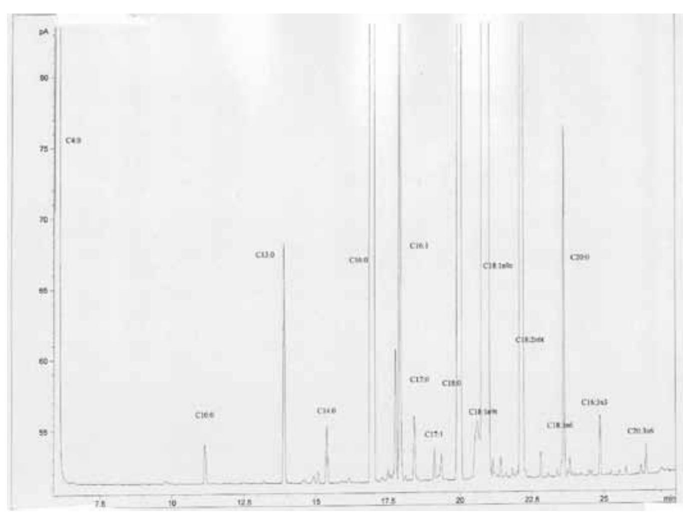

Figure 4: GC chromatogram for fatty acid methyl ester of fat emulsion which was used 5% in process

TABLE V

Contents of fatty acid methyl esters belong to natural fat (1) and fat(2) which was removed from parts of leather which was seen fatty spue(%)

Name of The Fatty Acid Methyl Ester	(1)	(2)
Myristic Acid Methyl Ester $C_{14:0}$	2.45	4.38
Myristoleic Acid Methyl Ester $C_{14:1}$	0.18	0.26
Pentadecanoic Acid Methyl Ester $C_{15:0}$	-	0.34
cis-10-Heptadecanoic Acid Methyl Ester $C_{15:1}$	-	0.45
Palmitic Acid Methyl Ester $C_{16:0}$	27.09	28.95
Palmitoleic Acid Methyl Ester $C_{16:1}$	3.32	1.86
Heptadecanoic Acid Methyl Ester $C_{17:0}$	0.18	0.98
cis-10-Heptadecenoic Acid Methyl Ester $C_{17:1}$	-	0.28
Stearic Acid Methyl Ester $C_{18:0}$	42.35	44.58
Linoleic Acid Methyl Ester $C_{18:1n9cis}$	16.55	14.78
Arachidic Acid Methyl Ester $C_{20:0}$		
cis-11-Eicosadienoic Acid Methyl Ester $C_{20:1}$	1.04	0.20
Linolenic Acid Methyl Ester $C_{18:3n3}$	-	0.36

1 Fatty Acid Methyl Ester contents of natural fat (%).

2 Fatty Acid Methyl Ester contents of fat leather which was seen fatty spue on surface (%).

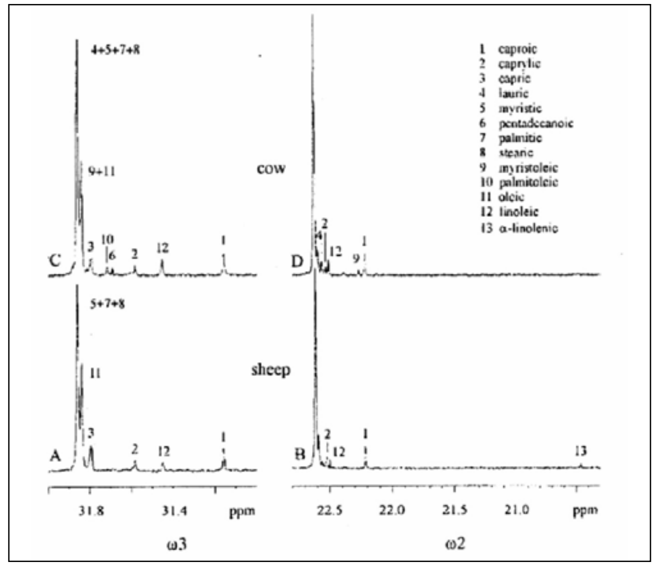

Figure 5: Identifications of the peaks of ^{13}C NMR spectra obtained by addition of standards[40] (Andreotti, G. et al., 2002)

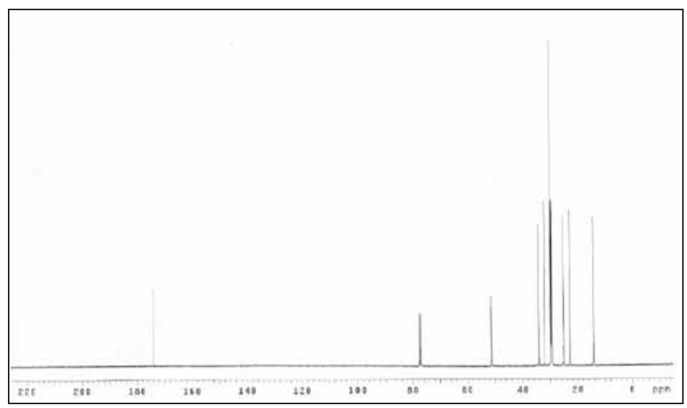

Figure 6: ^{13}C NMR spectra for palmitic acid

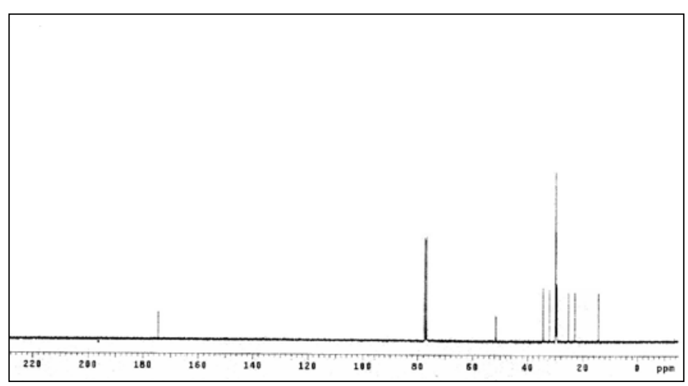

Figure 7: ^{13}C NMR spectra for stearic acid

This situation causes migration of fat or fatty substance towards to the leather surface.

When the chromatographs were examined at least thirteen fatty acid methyl esters were seen in the sheep skin fat and its emulsion. The ratio of the palmitic and stearic acids of fat emulsion was found higher than the natural fat. Also, the ratio of the palmitoleic and linoleic acid having unsaturated bonds were found less than the natural fat.

C Nuclear Magnetic Resonance (C-NMR) Analysis

Chemical shifts for varied C are reported in δ units, but the usual range is about 0 to 200 ppm downfield[40] (Figure 5).

C NMR spectrum of palmitic acid and stearic acid are represented in Figure 6 and Figure 7 respectively. C NMR spectra of natural fat and fat extracted from the fat spews area are shown in Figure 8 and Figure 9. In the region 176.0-174.0

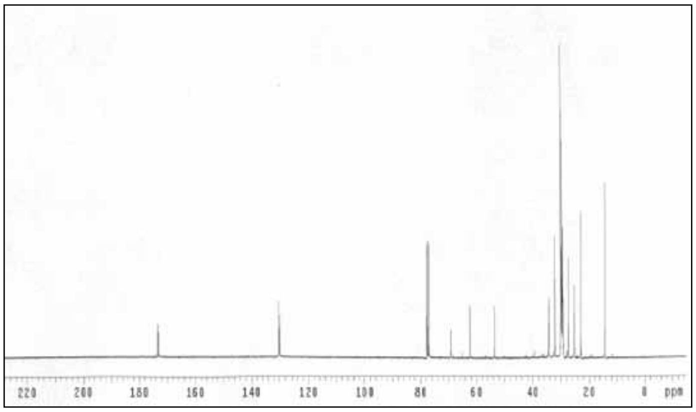

Figure 8: ^{13}C-NMR spectra for natural fat

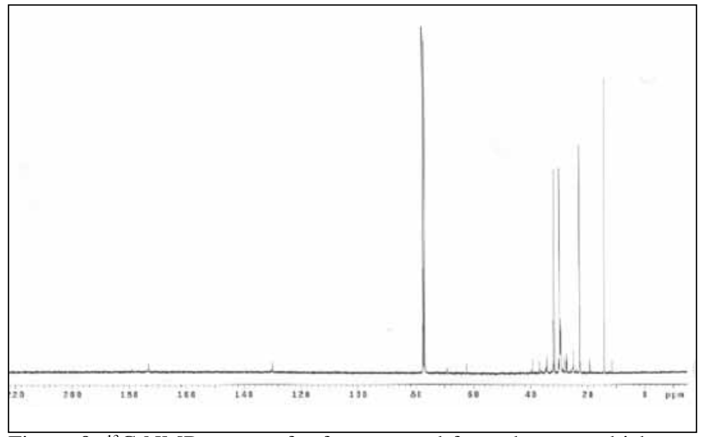

Figure 9: ^{13}C NMR spectra for fat extracted from the area which was seen fatty spue by solvent

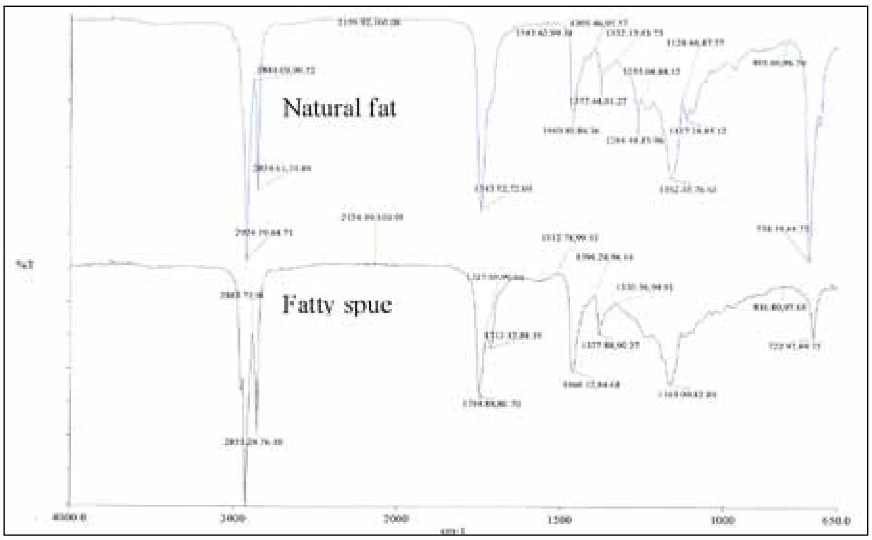

Figure 10: Overlay FTIR a spectra for natural fat with the sample extracted from the area which was seen fatty spue and transmittance ratios (T%).

ppm, signals correspond to different carbonyl carbons from fatty acids present in palmitic and stearic acid standard samples. In general, the chemical shift in this region depends on the type of glycerol ester (i.e., triacylglycerols, diacylglycerols, or monoacylglycerols), the stereo specific conformation position in acylglycerols), and the distance of the nearest double bond to the carbonyl carbon. [41]

The C NMR spectra of acylglycerols contain signals arising from the acyl chains and the glycerol carbon atoms. Resonances arising from the acyl chains can be divided into several groups, such as those from the carbonyl carbon, the α-carbon, and the olefinic carbons. When the spectrum is examined, a peak can be seen between 170 and 180 ppm due to high electronegativity. According to spectrum between 129.873 and 130.178 ppm, it may be concluded that natural fat emulsion has an unsaturated bond.

Fourier Transform Infrared Spectroscopy (FTIR)

In the present study description and evaluation of the application of FTIR spectroscopy in the determination of fats which are causing the fat spew problem to be the most efficient technique without titration because of its simplicity, rapidity, and efficiency. The spectrum showed in Figure 10 characteristics bands associated with common oil.[42] Comparison of overlaying format of the curves in Figure 10 and 11 show that changes in the absorption spectrum in all region of 3000-700cm^{-1} are clearly visible. FTIR spectra of natural fat and fat removed from fatty spewed area are presented in Figure 10. In this figure, the symmetrical pulsation of CH_2- is 2881.72-2854.29 cm^{-1}, deformation of CH_2 1460 cm^{-1}, valence of COO- 1395 and 1396 cm^{-1}, valence and deformation of C-O 1095 and 1330-1332 cm^{-1}, carbon skeleton 1045 and 1095 cm^{-1}, valence and deformation of C=O 1245 cm^{-1} and *cis* structure of the -C=C- bond between 3000 and 3400 cm^{-1}. FTIR spectrums of natural fat with fatty spew area fat sample and transmittance ratios of the FTIR spectrum have

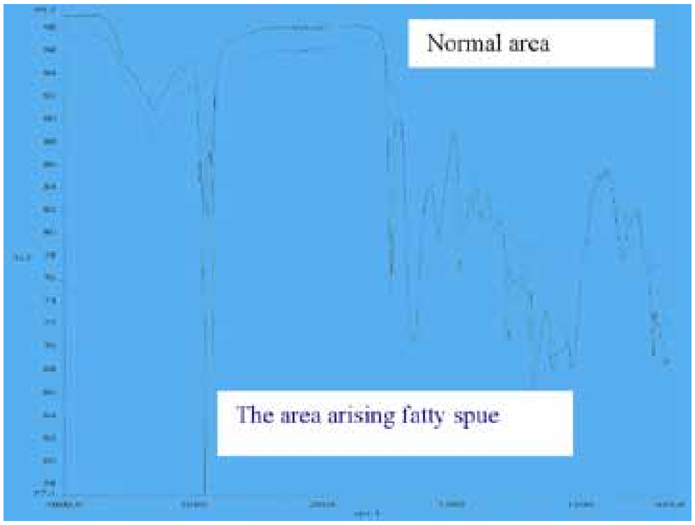

Figure 11: Overlay FTIR a spectrum of the normal area and the area which was arising fatty spue which is seen on the surface the same leather.

their own characteristic maximum absorption at 3000-2850cm^{-1} (CH_2) and 3383cm^{-1} (OH).[43] The FTIR spectrum shows strong absorption maxima for natural fat at 1743.52cm^{-1}, and 1460.80cm^{-1} which correspond to symmetrical and asymmetrical pulsations of the COO^- group. There are maxima also at 2924.19cm^{-1} 2881.09 and 2854.61 cm^{-1} which correspond to stretching pulsations of C-H links in hydrocarbon radicals. The absorption maximum OH groups and methylene are at 1370-722cm^{-1} in Figure 11.

Conclusions

There are various factors that cause fatty spew formation on leather surface and the characteristics of natural fat or fat emulsion is one the factors. Fat of fatty materials causing fatty spew problem generally cover the leather surface like a layer. This was experienced in the application of sample for the microscopy hen strict attention was paid not to remove the fatty layer from the leather surface. In addition, the SEM analysis system is able to analyze a sample by X-ray or atomic force sensor methods. In scanning electron microscopic studies, some difficulties may be experienced in sample preparation due to risk of removing fatty layer from surface of the leather. To have visual different visual supporting microscopy systems may also be required like an Atomic Force Microscopy.

According to the results, up to 3% of fat emulsion is usable as a fat emulsion in fatliquoring mixture, but at 5 and 7% levels it may cause a fat spew problem under selected storage conditions. Moreover, when chromatograms are examined it is seen that the leathers which are treated with 5 and 7% of natural fat emulsion have high amount of saturated fatty acid such as palmitic (C 16:0) and stearic acid (C 18:0) compared to the leather treated with 3% of natural fat emulsion. This spew was identified as a major fraction of palmitic acid and a minor fraction of stearic acid known as saturated fatty acids. These findings were supported with GC and NMR and FTIR analysis results. In view of these findings, it may be figured out that fat emulsions that do not include high numbered carbon may be used safely in the fatliquoring process and two fatty acids, palmitic and stearic acid, were found to be the main reasons for fatty spew formation. According to these findings unsaturated bonds of natural fat and fat emulsion have characteristic spectrums, but when these spectra were examined it can be seen that transmittance of unsaturated bonds for natural fat was higher than for fat emulsion. This means that unsaturated bonds containing fatty acids were saturated by chemicals like an oxidizing agent or other effects which were used in leather making processes.

Acknowledgement

This research was supported by Ege Univ. Scientific Research Project Department Directorate and Kasım Hilmi Utku Scientific Support Commission; part of the study was presented as visual display at the XXX. IULTCS Congress, 11-14 October, 2009, Beijing, China. The instrumental analyses were made by the equipment that was bought for the 2007DPT001 numbered project.

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